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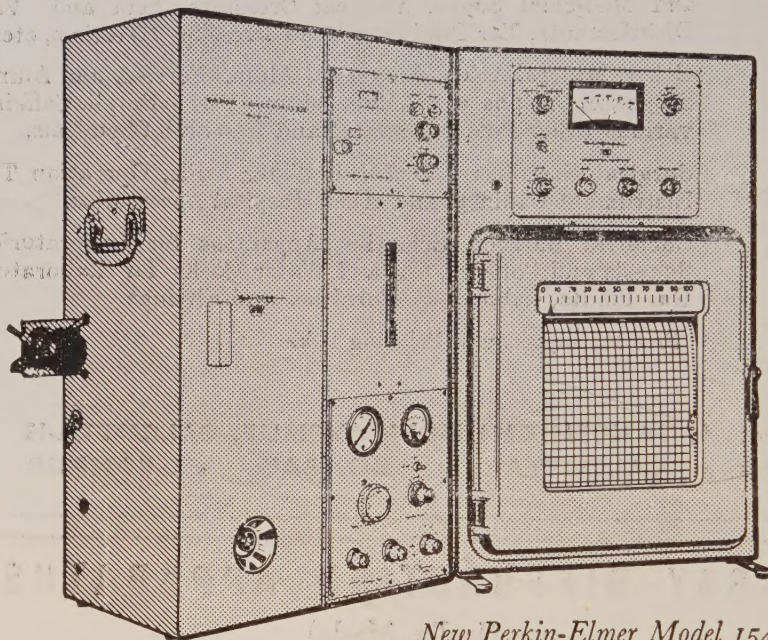
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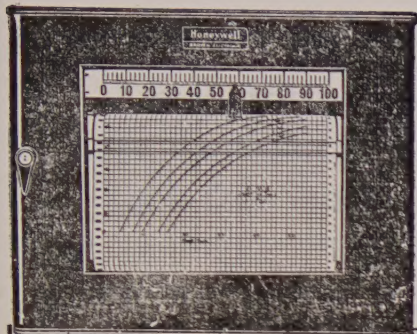
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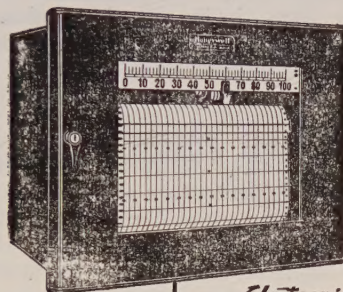
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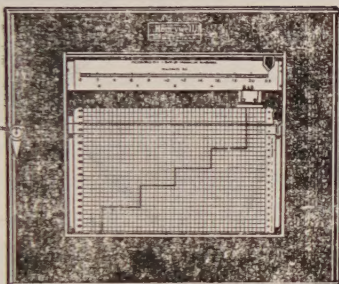
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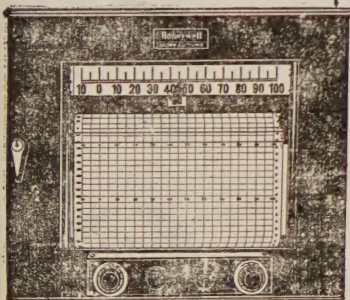
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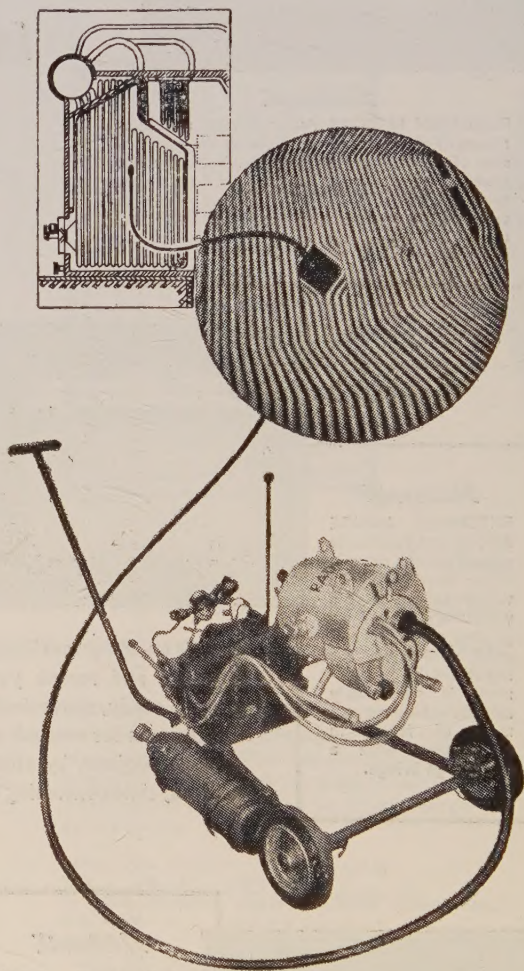


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APPLICATION OF THE UREY-BRADLEY AND THE ORBITAL VALENCY FORCE FIELDS TO SOME TETRAHEDRAL IONS

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ABSTRACT. In the case of the tetrahedral ions $\text{CrO}_4^{=}$, $\text{MoO}_4^{=}$, $\text{GaBr}_4^{=}$, $\text{InBr}_4^{=}$ and $\text{TlBr}_4^{=}$ the force constants have been calculated using the Urey-Bradley type of potential function and the orbital valency force field. The appropriate potential function for each case is discussed.

INTRODUCTION

Among the various types of potential functions used for studying the problem of molecular vibrations the valence force function is more extensively adopted than the others. Instead of a simple valence force function containing only quadratic terms, the one which takes into account the various interaction terms is found to be more satisfactory. However, a proper choice of these interaction terms or their adequate physical interpretation is not quite simple. A modification of the valence force function has been brought about by Urey and Bradley (1931) by introducing repulsion terms between non-bonded atoms of the type a/R^n where 'a' and 'n' are constants and R the distance between the atoms. A systematic investigation by Heath and Linnet (1948) on a number of tetrahedral halides of the group IV elements revealed that in a majority of cases n comes out to be nearly 4.5. This value was not acceptable for two reasons: (a) for the value $n = 4.5$ the stretching of the bonds would be more than what has been actually observed, (b) the Lennard-Jones (1924) relation $V = a/R^{12} - b/R^6$, for the inert gas atoms are more reasonable because the bonded halogen atoms resemble electronically the inert gas atoms. According to the Lennard-Jones function, n can be taken as 12 after neglecting the second term which corresponds to attraction and is small compared to the first term. The potential function consists of four constants, namely, the stretching constant K_1 , the bending constant K_α , $A \left(= \frac{1}{2} \frac{d^2 V}{dR^2} \right)$ and $\frac{B}{R} \left(= - \frac{1}{R} \frac{dV}{dR} \right)$ where V is the function mentioned above. The relation between A and B/R becomes fixed for any particular value of n , i.e., $A: B/R = n+1: 2$.

Another modification of the simple valence force field is what is known as the orbital valence force field first introduced by Heath and Linnet (1948). The

main feature of this function is that it makes use of the same constant for both the in plane and out of plane vibrations in the case of planar molecules and it differs from the simple valency force field only in its treatment of angular vibrations. According to Pauling's (1931) idea of directed valency the orbitals of an atom are set at definite angles to each other and the most stable bond between two atoms, say P and Q , is formed when one of the bond forming orbital of P overlaps to a maximum extent the bond forming orbitals of Q . Whenever there is a displacement from the maximum overlap during molecular vibrations restoring forces will be called into play and these can be assumed to be proportional to the displacements (which are of course small) if the vibrations are simple harmonic.

There are two ways by which the overlap of the bond forming orbitals can be increased during the vibrations. In the case of tetrahedral molecules or ions with which we are concerned here the orbitals of the central atom might be rotated as a whole in such a way as to improve the overlap. On the other hand, the orbitals of the central atom might change their hybridisation ratios by changing the angles at which they are set with each other so as to follow the movements of the outer atoms. This idea has been called orbital following.

The orbital valency force field without taking into account the idea of orbital following also consists of four constants K_1 , K_a' (instead of K_a as in the simple valency force field), A and B/R . Heath and Linnet (1948) have observed that for the ions ClO_4^- , SO_4^{2-} , SeO_4^{2-} and PO_4^{3-} the orbital valency force field is quite satisfactory. Such a force field is assumed in the present investigation to evaluate the force constants of the ions CrO_4^{2-} , MoO_4^{2-} , GaBr_4^- , InBr_4^- and TlBr_4^- .

THE POTENTIAL ENERGY FUNCTION

The potential energy function for tetrahedral molecules XY_4 can be written in the form

$$U = \sum_i f(r_i) + \sum_{i,j} F(R_{ij}) + \sum_{i,j} \frac{1}{2} K_a (\Delta\alpha_{ij})^2 \quad \dots (1)$$

the first term arising due to change in the $X-Y_i$ distance (r_i), the second term due to changes in the Y_i-Y_j distance (R_{ij}), and the last term due to changes in the angles $Y_iXY_j(\alpha_{ij})$. For small values of these variations the functions $f(r_i)$ and $F(R_{ij})$ can be expanded in powers of r_i and R_{ij} which denote the changes in r_i and R_{ij} from their equilibrium values r_i^0 and R_{ij}^0 . Retaining powers only up to the second we have

$$\begin{aligned} U = & \sum_i f(r_i^0) + \sum_i f'(r_i^0) \Delta r_i + \sum_i \frac{1}{2} f''(r_i^0) \Delta r_i^2 \\ & + \sum_{i,j} F(R_{ij}^0) + \sum_{i,j} F'(R_{ij}^0) \Delta R_{ij} + \sum_{i,j} \frac{1}{2} F''(R_{ij}^0) \Delta R_{ij}^2 + \sum_{i,j} \frac{1}{2} K_a (\Delta\alpha_{ij})^2 \quad \dots (2) \end{aligned}$$

Taking into consideration the above type of potential function the equations for the frequencies can be written as

I For the simple valency force field :

$$\text{Type } A_1 \quad \lambda_1 = \mu_y(K_1 + 8A) \quad \dots \quad (3)$$

Type T_2

$$\begin{aligned} \lambda_2 + \lambda_3 = (\mu_y + \frac{4}{3}\mu_x) & \left(K_1 + \frac{8}{3}A - \frac{4}{3}\frac{B}{R} \right) + (\mu_y + \frac{8}{3}\mu_x) \left(2K_\alpha + \frac{4}{3}A + \frac{10}{3}\frac{B}{R} \right) \\ & - \frac{8}{3}\mu_x \left(\frac{8}{3}A - \frac{4}{3}\frac{B}{R} \right) \quad \dots \quad (4) \end{aligned}$$

$$\begin{aligned} \lambda_2\lambda_3 = (\mu_y^2 + 4\mu_x\mu_y) & \left[\left(K_1 + \frac{8}{3}A - \frac{4}{3}\frac{B}{R} \right) \right. \\ & \left. \left(2K_\alpha + \frac{4}{3}A + \frac{10}{3}\frac{B}{R} \right) - \frac{1}{2} \left(\frac{8}{3}A - \frac{4}{3}\frac{B}{R} \right)^2 \right] \quad \dots \quad (5) \end{aligned}$$

$$\text{Type } E. \quad \lambda_4 = \mu_y \left(3K_\alpha + 2A + \frac{B}{R} \right) \quad \dots \quad (6)$$

II For orbital valency force field :

$$\text{Type } A_1 \quad \lambda_1 = \mu_y(K_1 + 8A) \quad \dots \quad (7)$$

Type T_2

$$\begin{aligned} \lambda_2 + \lambda_3 = (\mu_y + \frac{4}{3}\mu_x) & \left(K_1 + \frac{8}{3}A - \frac{4}{3}\frac{B}{R} \right) \\ & + (\mu_y + \frac{8}{3}\mu_x) \left(K'_\alpha + \frac{4}{3}A + \frac{10}{3}\frac{B}{R} \right) \\ & - \frac{8}{3}\mu_x \left(\frac{8}{3}A - \frac{4}{3}\frac{B}{R} \right) \quad \dots \quad (8) \end{aligned}$$

$$\begin{aligned} \lambda_2\lambda_3 = (\mu_y^2 + 4\mu_y\mu_x) & \left[\left(K_1 + \frac{8}{3}A - \frac{4}{3}\frac{B}{R} \right) \right. \\ & \left. \left(K'_\alpha + \frac{4}{3}A + \frac{10}{3}\frac{B}{R} \right) - \frac{1}{2} \left(\frac{8}{3}A - \frac{4}{3}\frac{B}{R} \right)^2 \right] \quad \dots \quad (9) \end{aligned}$$

$$\text{Type } E \quad \lambda_4 = \mu_y(K'_\alpha + 2A + \frac{B}{R}) \quad \dots \quad (10)$$

μ_x and μ_y denote the reciprocal of the masses of the atoms X and Y respectively and $\lambda_i = 4\pi^2 c^2 \nu_i^2$. If the interaction function between non-bonded-atoms is assumed as $V = a/R^n$

$$\text{then} \quad \frac{B}{R^0} = \frac{na}{(R^0)^{n+2}} \quad \text{and} \quad A = \frac{n(n+1)a}{2(R^0)^{n+2}}$$

so that

$$\frac{A}{(B/R^0)} = \frac{n+1}{2}$$

EVALUATION OF THE CONSTANTS

The values of K_a and K_a' can be obtained in terms of A from the equation for the doubly degenerate frequency λ_4 . These can be then substituted in the first equation for the triply degenerate vibrations T_2 which will give an equation in K_1 and A which can be solved simultaneously with the equation for the totally symmetric class A_1 . By substituting the values of the force constants in the second equation for T_2 , the calculated and observed values of $\lambda_2\lambda_3$ can be compared.

RESULTS

The fundamental frequencies of the ions are taken from the published results on their Raman spectra and they are given in Table I. In Table II to V the values of the force constants for the six ions have been given while Table VI contains the observed and calculated values of $\lambda_2\lambda_3$. All the force constants are given in 10^5 dynes/cm.

TABLE I
Frequencies in cm^{-1}

Ion	$\nu_1(A_1)$	$\nu_2(T_2)$	$\nu_3(T_2)$	$\nu_4(E)$	Reference
$\text{CrO}^=4$	858	510	875	485	Landolt Bornsteins's Tables, 1953
$\text{MnO}^=4$	940	365	895	220	
$\text{GaBr}^=4$	210	102	278	71	Woodward and Nord, (1955)
$\text{InBr}^=4$	197	79	239	55	Woodward and Bill, (1955)
$\text{TlBr}^=4$	190	64	209	51	Rolfe, Sheppard and Woodward (1954)

TABLE II
S.V.F.F. $n = 4.5$

Ion	K_1	A	B/R	K_a
$\text{CrO}^=4$	4.209	0.3416	0.1242	0.4703
$\text{MoO}^=4$	5.503	0.3536	0.1286	0.0634
$\text{GaB}^=4$	1.269	0.101	0.0367	-0.0004
$\text{InBr}^=4$	1.307	0.0654	0.0237	-0.004
$\text{TlBr}^=4$	1.26	0.055	0.02	-0.0024

TABLE III
S.V.F.F. $n = 12$

Ion	K_1	A	B/R	K_α
$\text{CrO}_4^{=}$	4.466	0.3095	0.0476	0.517
$\text{MoO}_4^{=}$	5.73	0.3252	0.05	0.1085
$\text{GaBr}_4^{=}$	1.054	0.1278	0.0197	-0.0126
$\text{InBr}_4^{=}$	1.365	0.058	0.009	0.0058
$\text{TlBr}_4^{=}$	1.303	0.0495	0.0076	0.0053

TABLE IV
O.V.F.F. $n = 4.5$

Ion	K_1	A	B/R	K_α'
$\text{CrO}_4^{=}$	3.50	0.43	0.1564	1.201
$\text{MoO}_4^{=}$	5.408	0.3654	0.1328	0.1623
$\text{GaBr}_4^{=}$	1.269	0.1009	0.0367	-0.0011
$\text{InBr}_4^{=}$	1.313	0.0646	0.0235	-0.012
$\text{TlBr}_4^{=}$	1.263	0.0545	0.0198	-0.0063

TABLE V
O.V.F.F. $n = 12$.

Ion	K_1	A	B/R	K_α'
$\text{CrO}_4^{=}$	3.741	0.4	0.0615	1.3568
$\text{MnO}_4^{=}$	5.581	0.3438	0.0529	0.2856
$\text{GaBr}_4^{=}$	1.345	0.0915	0.014	0.0404
$\text{IdBr}_4^{=}$	1.357	0.059	0.009	0.0153
$\text{TlBr}_4^{=}$	1.296	0.0504	0.0078	0.0139

TABLE VI

Ion	$\frac{\lambda_2\lambda_3}{\mu_y^2 + 4\mu_x\mu_y}$		$\frac{\lambda_2\lambda_3}{\mu_y^2 + 4\mu_x\mu_y}$ calculated		O.V.F.F.	
	observed	S.V.F.F. $n = 4.5$	$n = 12$	$n = 4.5$	$n = 12$	
$\text{CrO}_4^{=}$	7.936×10^{10}	8.691×10^{10}	8.105×10^{10}	9.754×10^{10}	9.41×10^{10}	
$\text{MoO}_4^{=}$	5.692×10^{10}	6.146×10^{10}	5.017×10^{10}	6.461×10^{10}	5.557×10^{10}	
$\text{GaBr}_4^{=}$	3.195×10^9	3.573×10^9	2.391×10^9	3.755×10^9	3.033×10^9	
$\text{InBr}_4^{=}$	2.085×10^9	2.1948×10^9	1.693×10^9	2.117×10^9	1.763×10^9	
$\text{TlBr}_4^{=}$	1.545×10^9	1.792×10^9	1.379×10^9	1.761×10^9	1.444×10^9	

It can be seen from Table VI that in the case of MoO_4 , GaBr_4 and TlBr_4 the orbital valency force field with $n = 12$ is more satisfactory than the others while for InBr_4 the same field with $n = 4.5$ instead of 12 suits better. For the chromate ion the simple valency force field with $n = 12$ yields better results than the others. This simple valency force field with $n = 4.5$ is least satisfactory for all the ions. In the case of the ions ClO_4^- , SO_4^{2-} , SeO_4^{2-} and PO_4^{3-} , Heath and Linnet (1948) have observed that the orbital valency force field holds better. The difference between observed and calculated values of $\lambda_2\lambda_3$ can be further reduced by introducing modifications such as orbital following.

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X-RAY STUDY OF A DEHYDRATED PHASE OF COPPER AMMONIUM SULPHATE HEXAHYDRATE

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Plate X

ABSTRACT. The cell-dimensions of $\text{Cu}[(\text{NH}_4\text{SO}_4)]_2 \cdot 6\text{H}_2\text{O}$ (monoclinic, space-group $\text{P2}_1/a$) as determined from rotation photograph are found to be $a = 9.27\text{\AA}$, $b = 12.50\text{\AA}$, $c = 6.33\text{\AA}$ $\beta = 106^\circ 5'$, with 2 molecules per unit cell. The results have been utilised to index the powder pattern of the substance. Analysis of the powder pattern by Lipson's method of the first stage dehydration product, $\text{Cu}[\text{NH}_4(\text{SO}_4)]_2 \cdot 2\text{H}_2\text{O}$ formed at 65°C shows that the product has orthorhombic structure, the cell dimensions being $a = 14.84\text{\AA}$, $b = 12.52\text{\AA}$, $c = 10.69\text{\AA}$. The probable space groups are $\text{Pmn } 2_1$ and Pmnm with 8 molecules per unit cell.

INTRODUCTION

Magnetic measurements of the single crystals of a large number of Tutton salts (general formula $\text{M}(\text{RXY}_4)_2 \cdot 6\text{H}_2\text{O}$ where $\text{M} = \text{Mg, Zn, Cd, Cu, Ni, Co, Fe, etc.}$ $\text{R} = \text{K, Rb, Cs, NH}_4$, $\text{XY}_4 = \text{SO}_4, \text{SeO}_4$ or BeF_4) showed (Bose *et al.* 1957 and 58) that they lose their magnetic anisotropies in the range $338^\circ - 393^\circ\text{K}$ the exact temperature depending upon the particular salt. This is evidently due to changes in crystal structure accompanying loss of water of crystallisation which causes the single crystals to become polycrystalline. Since the crystalline magnetic properties are intimately connected with the structure it would be interesting to study these changes in structure in order to elucidate the changes in the magnetic properties. As a typical case, the thermal dehydration of $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ was undertaken and the corresponding changes in crystal structure investigated.

2. X-RAY MEASUREMENTS ON $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$

X-ray data on single crystals of $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ is lacking, though one of the isomorphous salts $\text{Mg}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ has been studied using trial and error method by Hofmann (1931). By analogy with the latter it follows that $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ is also monoclinic having 2 molecules in the unit cell and belongs to

the space-group $P2_1/a$. We have determined the dimensions of the unit cell from rotation photographs about the three crystallographic axes. They are

$$a = 9.27 \text{ \AA}$$

$$b = 12.50 \text{ \AA}$$

$$c = 6.33 \text{ \AA}$$

$$\beta = 106^\circ 5'.$$

The monoclinic angle β is found from the zero layer-line of the rotation photograph about b -axis.

A powder diffraction pattern has also been taken at room-temperature and the spacings indexed with the help of the above values of cell dimensions.

TABLE I

$d\text{\AA}$	Intensity	$1/d^2$ observed	$1/d^2$ calculated	Indices
7.193	vw	0.0193	0.0190	110
6.105	ms	0.0268	0.0270	001
5.456	ms	0.0336	0.0334	011
5.129	w	0.0380	0.0384	120
4.418	w	0.0502	9.0504	200
4.188	vs	0.0570	0.0568	210
3.759	vs	0.0708	0.0702	130
3.620	w	0.0763	0.0758	220
3.386	ms	0.0872	0.0870	$13\bar{1}$
3.061	s	0.1067	0.1066	112
2.486	s	0.1235	0.1239	212
2.715	w	0.1357	0.1353	321
2.556	m	0.1531	0.1528	240
2.441	s	0.1678	0.1673	$33\bar{1}$
2.229	ms	0.2013	0.2017	400
2.176	w	0.2112	0.2104	$042]$
			0.2104	$250]$
2.144	w	0.2175	0.2170	$25\bar{1}$
2.097	ms	0.2274	0.2273	420
2.031	w	0.2424	0.2431	003
1.963	w	0.2595	0.2593	430
1.922	ms	0.2707	0.2712	$31\bar{3}$
1.858	w	0.2897	0.2897	$233]$
			0.2893	$312]$
1.816	w	0.3032	0.3040	440
1.768	w	0.3200	0.3206	510
1.736	w	0.3318	0.3312	351
1.701	w	0.3456	0.3454	043

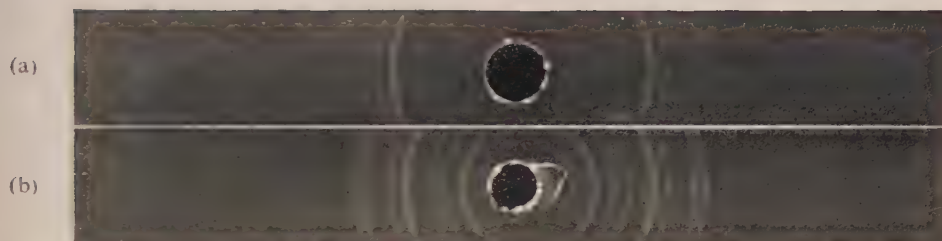


Fig. 1. Debye-Scherrer patterns

- (a) Copper ammonium sulphate hexahydrate $\text{Cu} [(\text{NH}_4) \text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$
(b) Copper ammonium sulphate dihydrate $\text{Cu} [(\text{NH}_4) \text{SO}_4]_2 \cdot 2\text{H}_2\text{O}$



The conditions of reflection satisfied are :

hkl : no condition

$h0l$: $h = 2n$.

There is no powder-line with $0k0$ reflection. But rotation photographs show that for $0k0$, $k = 2n$ spots are present. Hence the space-group is $P 2_1/a$ which supports the earlier assumptions.

STUDIES ON THE DEHYDRATION PRODUCT

Next powdered sample of $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ of weighed quantity is heated automatically controlled thermostatic oven and the loss of weight at different temperatures is determined. At 338°K it shows an abrupt loss of weight which corresponds to 4 molecules of water. When the temperature is brought down the sample soon regains its original weight. It indicates that $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ undergoes a reversible transformation to a dihydrate at 65°C . This is also evident from the X-ray powder pictures.

It is interesting to study the structure of the dehydrated product. Since the dehydrated powder absorbs moisture rather quickly, instead of packing the dehydrated powder in capillary tubes in the usual way, the capillary tube is first packed with finely powdered $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$, now the fine tube packed and open at both ends is heated in the oven at a constant temperature somewhat above 65°C for 24 hours when it attains constant weight.

The capillary tube is now quickly sealed at both ends so that the treated sample does not come in contact with moisture from the atmosphere. The sample is mounted in a camera of 57.3 mm radius and X-ray powder photograph is taken with CuK_α radiation from a Raymax 60 Diffraction unit running at 50KV and 10 mA. The powder pattern thus obtained is entirely different from that for $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$. Besides, the spacings measured for the powder-line has no spacing common with the known spacings of either of $(\text{NH}_4)\text{SO}_4$ or CuSO_4 (anhydrous) or $\text{CuSO}_4 \cdot \text{H}_2\text{O}$. This shows that the dehydrated product is a new double salt having a unique crystal structure. If the dehydrated powder is cooled to room-temperature in contact with atmosphere and photograph taken, the original powder pattern of $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ is obtained. The powder photograph is the only source of information regarding the structure of the new compound since, in spite of many attempts the substance could not be obtained as single crystals from aqueous medium. Hence attempt has been made to index the powder-photograph taking the substance to have the molecular formula $\text{Cu}[(\text{NH}_4)\text{SO}_4]_2 \cdot 2\text{H}_2\text{O}$.

First attempts were made to index the powder lines in terms of cubic, tetragonal and hexagonal system. Since the data do not fit with either of these systems Lipson's method (Lipson, 1949) was applied to find if the crystal belongs to the

orthorhombic system. For orthorhombic system, $\sin^2 \theta$ values obtained from each pair of Debye-Scherrer ring can be written as

$$\sin^2 \theta_{hkl} = \frac{\lambda^2}{4a^2} h^2 + \frac{\lambda^2}{4b^2} k^2 + \frac{\lambda^2}{4c^2} l^2$$

$$= Ah^2 + Bk^2 + Cl^2 \quad \text{where} \quad A = \frac{\lambda^2}{4a^2} \quad B = \frac{\lambda^2}{4b^2} \quad C = \frac{\lambda^2}{4c^2}$$

TABLE II

dÅ	Intensity	$\sin^2 \theta$ observed	$\sin^2 \theta$ calculated	Indices
12.199	w	0.0039	0.0038	010
8.023	s	0.0092	0.0090	011
6.193	s	0.0155	0.0152	020
5.771	w	0.0178	0.0179	120
5.345	s	0.0209	0.0208	002
4.551	w	0.0287	0.0282	310
4.331	vs	0.0317	0.0312	221
4.312	vs	0.0319	0.0316	202
3.952	ms	0.0381	0.0387	122
3.785	ms	0.0415	0.0421	131
3.642	w	0.0448	0.0447	321
3.508	w	0.0483	0.0484	401
			0.0488	312
3.364	vw	0.0525	0.0522	411
3.268	vs	0.0557	0.0550	032
3.226	vs	0.0571	0.0577	132
3.150	m	0.0599	0.0603	311
3.064	vs	0.0631	0.0635	140
3.033	vs	0.0646	0.0640	402
			0.0647	132
2.960	w	0.0679	0.0678	412
2.885	w	0.0714	0.0713	510
2.447	ms	0.0788	0.0792	422
			0.0793	332
2.657	ms	0.0842	0.0843	142
2.514	w	0.0904	0.0898	114
2.495	w	0.0955	0.0950	050
2.450	s	0.0990	0.0984	024
2.298	w	0.1126	0.1124	610
2.139	s	0.1299	0.1302	414
2.081	s	0.1373	0.1368	060
			0.1365	115
1.983		0.1511	0.1508	443
1.922		0.1609	0.1611	360
1.762	ms	0.1915	0.1010	016
1.730	ms	0.1986	0.1983	741
1.521	w	0.2571	0.2575	107
1.497	w	0.2653	0.2661	715

The values of $\sin^2 \theta_{hkl}$ known as q -values observed from the pattern are listed in Table II. With the above values of $\sin^2 \theta$, the difference diagram is drawn according to Lipson's method. The diagram shows frequently-occurring values

from which the values of the constants A, B, C are determined in the following way.

If we choose the first three values of Δq from the Lipson's chart i.e., 0.0028, 0.0038, 0.0052, we find that (1) the 4 fold and 9 fold multiples of A i.e., .0110, .0250 are present, (2) the 4 fold, 9 fold, 16 fold multiples of B i.e., 0.0152, 0.0340, 0.061 are frequently occurring, (3) the 9 fold, 16 fold and 25 fold multiples of C i.e., 0.046, 0.083 and 0.1300 are also present in the chart.

There are no other value of Δq in the Lipson's chart which has so many multiples present. So these are the most probable values of constants A, B, C . With these values of A, B, C all the values of $\sin^2\theta_{hkl}$ in Table II can be successfully indexed. For better adjustment A is taken as 0.0027 and the agreement between the observed and calculated values is highly satisfactory, the discrepancy lying within experimental errors. So it is concluded that the crystal belongs to the orthorhombic system, with the dimensions of the unit cell as calculated from A, B, C

$$a = 14.84 \text{ \AA}$$

$$b = 12.52 \text{ \AA}$$

$$c = 10.69 \text{ \AA}.$$

Measurement of the density of the dihydrate is very difficult since it always tends to be converted into the hexahydrate when exposed to atmosphere. The hexahydrate powder is taken in a specially designed pyknometer and treated in the furnace at 70°C for about 24 hours so that the dihydrate is obtained. The pyknometer is cooled in a dessicator and weighed. Since the substance is highly soluble in water its density is measured with respect to paraffin oil of known density. Repeated measurements show that the density of the dihydrate is 2.04 gm/c.c.

With this value of density and the dimensions of the unit cell given above, the number of molecules per unit comes out as $7.50 \approx 8$. The agreement is satisfactory in view of the fact that due to the extreme instability of the dihydrate, at room temperature, sufficient accuracy cannot be obtained in the determination of the density. This integral value also supports the choice of the unit cell of the crystal.

The conditions limiting possible reflections indicated by Table II are

hko : no condition

okl : no condition

hol : $h+l = 2n$

hko : no condition

hoo : $h = 2n$.

oko : no condition

ool : $l = 2n$.

The conditions agree with both the space groups P_{mn2_1} and P_{mnm} . Since the substance has not yet been obtained in the single crystal form it is not possible to ascertain the space-group uniquely from single crystal photograph.

4. DISCUSSIONS

It is interesting to note that the orientation of the crystalline principal magnetic axes in the (010) plane of the crystal of $\text{Cu}[(\text{NH}_4\text{SO}_4)]_2 \cdot 6\text{H}_2\text{O}$ changes by about 19° in the range 90°K to 338°K slowly at first and then rapidly as the transition temperature of 338°K is approached. Correspondingly the relative orientation between the approximate tetragonal axes of the two equivalent $\text{Cu}^{2+} \cdot 6\text{H}_2\text{O}$ octahedra equally inclined to the b -axis of the unit cell, change by about 10° (Bose *et al*, 1957). This indicates that even before the transition temperature is reached a rapid rearrangement of the constituents of the unit cell is taking place, owing to increased thermal motions, tending to make the four water molecules of coordination redundant for the stable equilibrium of the lattice at the transition point, which becomes apparent by the fact that as soon as this temperature is reached these water molecules are thrown out of the lattice and the constituents of the unit cell assume the new symmetry of the orthorhombic class for the dihydrate. The manner of reorientation by rotation of the $\text{Cu}^{2+} \cdot 6\text{H}_2\text{O}$ groups about the b -axis previous to transition and the X-ray finding that the b -axial lengths of the hexahydrate and dihydrate are equal seem to indicate that there is a correspondance between the b -axes of the monoclinic and the orthorhombic varieties. Also the transition from monoclinism to orthorhombicity is attained at the transition temperature by a continuous approach of the a and c axes of the monoclinic cell towards orthogonality.

More X-ray data on the structure of the salt before and after transition would verify the predictions and attempts are being made to obtain these.

ACKNOWLEDGMENT

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THE CRYSTALLITE ORIENTATION IN MESTA FIBRE

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ABSTRACT. The orientations of crystallites in mesta fibres raw, delignified and treated with different concentrations of caustic soda have been studied. The Hermans' orientation factor, the average angle of orientation and angle for 40% intensity for five samples have been determined from intensity distribution curves of the equatorial arcs in the X-ray diffraction photographs. It has been observed that for mesta, the average angle of orientation varies from 11° to 14° and Hermans' orientation factor varies from 0.91 to 0.94.

INTRODUCTION

Mesta, a substitute fibre for jute, has its crystalline structure similar to that of jute. It has been established that in jute fibres, the crystallites have their 'b' axis nearly parallel to the fibre axis making a small angle. The other axes of the crystallites are randomly oriented. The average angle of orientation is generally measured from the distribution of intensity along the arcs into which the diffraction spots are drawn. These have been measured for cotton, jute, ramie etc. The relation between orientation and physical properties for cotton has been studied by many workers. Sen and Wood (1949) studied the orientations for jute and ramie. They compared Hermans' orientation factor and half maximum intensity angle for jute and ramie. They also observed a difference in orientation factors for different varieties of jute.

The present work was undertaken in order to study the orientation factor for mesta fibre and compare it with established values of cotton, jute and ramie, and also to investigate the variation in orientations in the raw and delignified fibres and fibres treated with different strengths of caustic soda. The Hermans' orientation factor, the average orientation angle and angle for 40% intensities were determined.

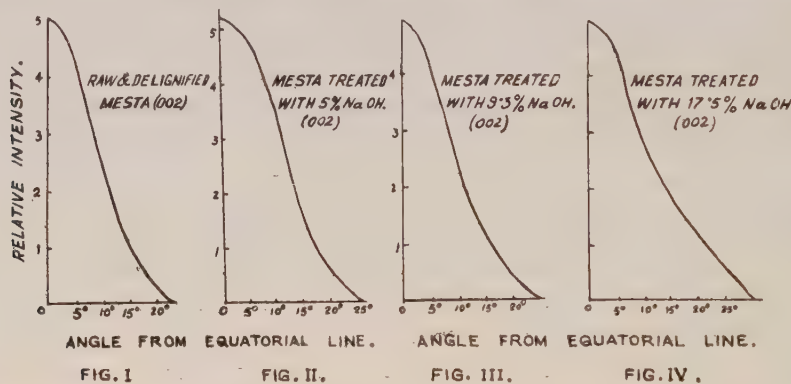
PROCEDURE

Samples of alkali treated fibres were prepared by treating raw mesta fibre with different strengths of NaOH solution. Delignified samples were prepared in the usual way by the 'Textone' process. X-ray diffraction photographs were taken for all samples with CuK_α radiation (nickel filtered) from a Hadding type

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X-ray tube. The camera used was a flat cassette plate camera. Photographs of moderate intensity suitable for microphotometer work were taken.

Following Hermans *et al.* (1939) a series of microphotometer curves of (002) and composite (101) and (10 $\bar{1}$) interferences were recorded starting from the equatorial lines of the diffraction photographs and proceeding in radial lines at angular intervals of 2°30'. Densities of the photometer curves were converted into intensities from a density—log intensity curve, drawn experimentally by comparison with the curve of a standard calibration strip having intensities at various points proportional to the distance from zero intensity point. From these, curves were drawn for intensities against angular distances with equatorial lines for the (002)



reflections. The curves are shown in Figs. I-IV. These intensity distribution curves represent the statistical distribution of the paratropic planes of the crystallites of the fibres. Intensity may be designated by $I = F(\alpha)$ where α is the angular distance from the equator. According to Hermans the average angle of orientation α_m is given by

$$\overline{\sin^2 \alpha_m} = \overline{\sin^2 \alpha_1} + \overline{\sin^2 \alpha_2}$$

$$\overline{\sin^2 \alpha_1} = \frac{\int_0^{\pi/2} F(\alpha_1) \sin^2 \alpha_1 \cos \alpha_1 d\alpha_1}{\int_0^{\pi/2} I \cos \alpha_1 d\alpha_1}$$

and

$$\overline{\sin^2 \alpha_2} = \frac{\int_0^{\pi/2} F(\alpha_2) \sin^2 \alpha_2 \cos \alpha_2 d\alpha_2}{\int_0^{\pi/2} I \cos \alpha_2 d\alpha_2}$$

and the Hermans' orientation factor

$$f_x = 1 - \frac{3}{2} \overline{\sin^2 \alpha_m}$$

In the case of raw fibres, it has been found that $F(\alpha_1) = F(\alpha_2)$; hence only $F(\alpha)$ for (002) is shown in the curves. (Only for the case of fibres treated with

17.5% NaOH both the (002) and (101) (Fig. 5) reflections were taken into consideration for calculating α_m and f_x . Empirical intensity curves were drawn

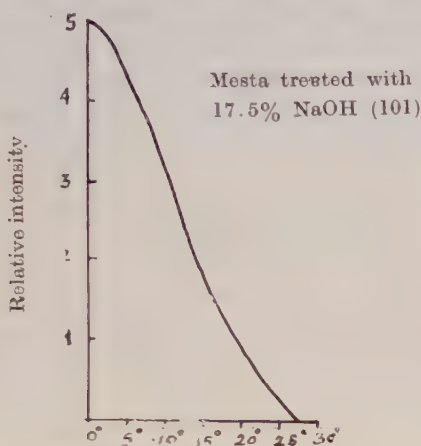


Fig. V. Angle from equatorial line.

by plotting the values of $I \sin^2 \alpha \cos \alpha$ and $I \cos \alpha$ against angular distances and the usual method of graphical integration of both curves were done. The ratio of integrals were then found out. From these, $\overline{\sin^2 \alpha_m}$ were determined and from them α_m and f_x were evaluated. Values of angles at 40% intensity were also determined from the intensity distribution curves.

RESULTS AND DISCUSSION

In Table I are given the values of f_x , α_m and angle at 40% intensity in the intensity distribution curves for (002) reflections. The results obtained show that the average angle of orientation α_m and f_x do not change substantially till

TABLE I

Showing the average angle of orientation, 40% intensity angle and Hermans' orientation factor

Sample	Average angle of orientation	40% intensity angle	Hermans' orientation factor
Raw mesta	11.6°	11.0°	0.940
Delignified mesta	11.6°	11.0°	0.940
Raw mesta treated with 5% NaOH	10.5°	10.8°	0.950
Raw mesta treated with 9.3% NaOH	12°	11.0°	0.935
Raw mesta treated with 17.5% NaOH	14.86° (002) 14.14° (101)	15.0° (002) 14.0° (101)	0.900 0.910
			0.905

treatment with 9.3% NaOH, but for samples treated with 17.5% NaOH, the values obtained differ considerably from the former ones.

The average angle of orientation α_m and orientation factor f_x for raw mesta are found to be $\alpha_m = 11.60$ and $f_x = 0.94$, whereas the average angle for jute fibres varies from 8° to 9° approximately and f_x varies from 0.96 to 0.97 as determined by Sen and Chowdhury (1957). In the case of ramie these are given by $7^\circ 36'$ and 0.973 (Hermans).

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THE DIELECTRIC PROPERTIES OF ROSIN-MALEIC ANHYDRIDE RESIN

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ABSTRACT. The dielectric properties of rosin-maleic anhydride resin have been measured over the temperature range of 25°C to 170°C and the frequency range of 1 Kc/s to 500 Kc/s. Within this range of temperature and frequency it behaves as a polar resin in the anomalous dispersion range. Its dielectric constant vs temperature curve shows however a peculiar behaviour at high temperatures. At about 150°C dielectric constant values attain a maximum after gradually rising with temperature in the normal way of polar resins. But above this temperature a sudden and steep rise in the permittivity is observed. An attempt has been made to explain this peculiarity on the basis of its estimated rotor dimension and infrared absorption spectrogram.

INTRODUCTION

Rosin plays an important part in the production of several semi-synthetic resins. It is widely used as a modifier in the production of so-called modified synthetic resins, such as rosin modified phenol formaldehyde resins or alkyds. Another type of synthetic resin derived from rosin is the rosin-maleic anhydride adduct formed by the method of Diels-Alder reaction known as the "diene synthesis". This method of synthesis involves a "diene" system i.e. a system having conjugated double bonds reacting with a component having an ethylenic linkage flanked by carbonyl or carboxyl groups in such a manner that the "diene" system opens up and the terminal carbons become affixed at the double bond of the ethylenic linkage.

The chemical structure of rosin or abietic acid shows that it possesses a conjugated system of double bonds and consequently it reacts with maleic anhydride giving an addition compound. In fact, this diene synthesis confirms the presence of the conjugated double bonds in the structure of the abietic acid molecule. It should be noted that this compound is the partial anhydride of a tribasic acid and hence its acid value must be reduced and this is usually done by esterification with any polyhydric alcohol like glycerol, mannitol, pentaerythritol etc.

Now X-ray studies on the rosin maleic-anhydride resins and ester gum by Beal and co-workers (1932) have revealed that they show precisely the same

rings which are associated with raw rosin. Esterification with glycerol or reacting it with maleic anhydride does not change its inherent character.

Because of the large size of the esterified rosin-maleic anhydride molecule, its rotation as a whole, when placed in the rapidly alternating electric field, is unlikely. Obviously, if dielectric loss occurs due to orientation it may only be due to contributions from side groups attached to the main molecule. Although rosin has been found to be present in this resin as a constituent unit, its freedom of rotation has been severely restricted by a pair of carbon-carbon bonds with the maleic anhydride on the one hand and by its linkage with the pentaerythritol molecule through the esterification of its carboxyl group on the other.

From a previous study of the dielectric properties of rosin it has been observed by the authors (Sen and Bhattacharya, 1958b) as well as by Kitchin and Muller (1928) that the dimension of its rotating unit is about 4.6\AA which is in close agreement with the actual dimension of the abietic acid molecule calculated on the basis of its accepted chemical structure. This agreement led the authors to the obvious conclusion that the rotation of the entire abietic acid molecule was responsible for its dielectric behaviour. But a similar study in the case of ester gum (Sen and Bhattacharya, 1958a) or copal ester (Sen and Bhattacharya, 1960) revealed a different story. In both the cases the dimensions obtained for the rotating units were exactly the same as that of a hydroxyl group. The presence of hydroxyl groups in these resins was also confirmed from their infra-red absorption spectrograms. These evidences tend to suggest that instead of the whole molecule the hydroxyl groups in these resins are probably the rotating units. Hence it is inferred that when molecules of abietic acid (rosin) or copalic acid (copal) combine (e.g., by esterification with glycerol) to form larger molecules, their rotation as a whole is restricted and only the rotation of smaller groups can occur in the investigated range of frequency. In this context it is therefore of interest to study the dielectric properties of rosin-maleic anhydride adduct in relation to those of rosin and obtain the dimension of its rotating units.

EXPERIMENTAL

The same experimental procedure as was followed in the case of other resins and the details of which appeared elsewhere (Sen and Bhattacharya, 1958a, 1958b) has been employed. The sample used in this investigation was a pentaerythritol ester of the rosin-maleic anhydride adduct manufactured by the Imperial Chemical Industries Ltd., London, and sold under the trade name of Bedesol-74.

The results of measurements of dielectric constant ϵ' , dielectric loss ϵ'' and power factor $\tan \delta$ at different temperatures and frequencies are shown graphically in Figs. 1, 2 and 3. Quite contrary to our expectation, these graphs give clear evidence of the typical polar nature of this resin. The loss factor-temperature and the power factor-temperature curves shown in Figs. 2 and 3, are the usual absorption curves of a polar material. These curves begin to rise at a compara-

tively higher temperature viz, about 100°C for almost all the frequencies except that of 1 Kc/s. The loss peaks are also more or less of the same heights.

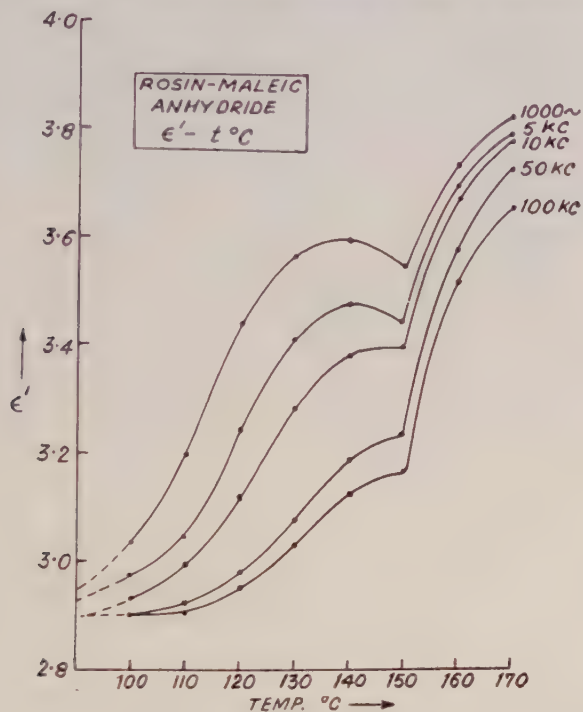


Fig. 1

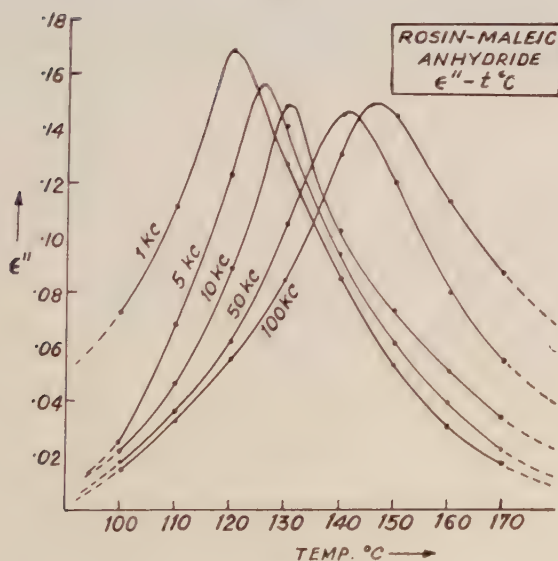


Fig. 2

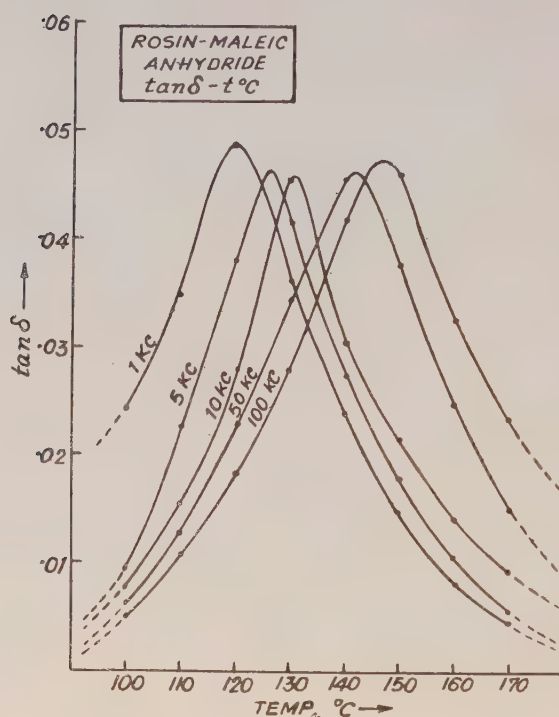


Fig. 3

But the dielectric constant-temperature graphs show a peculiar behaviour. It may be noticed from Fig. 1 that the permittivity for all the frequencies begins to rise from about 100 $^{\circ}\text{C}$ in the usual way and attains a maximum at temperatures between 130 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$. But peculiarly enough, after 150 $^{\circ}\text{C}$ it is found to make

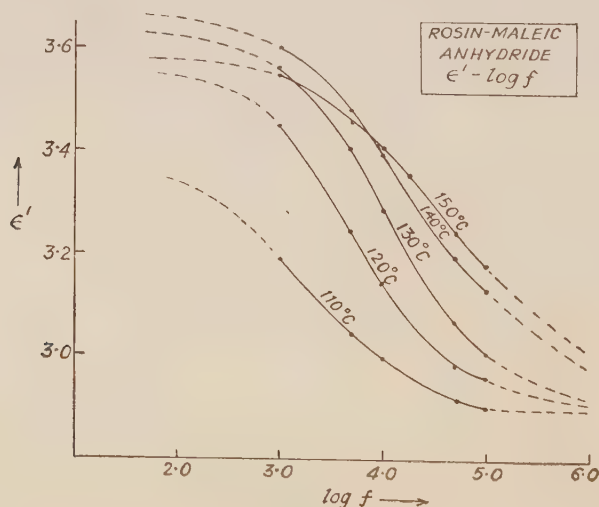


Fig. 4

a sudden and steep rise again. Measurements were carried out up to 170°C only as it was apprehended that the resin might polymerize after that temperature. This peculiar behaviour can only be explained on the supposition that at temperatures higher than 150°C the resin becomes unstable and more and more dipoles are somehow set free which now increase the orientation polarization and make the permittivity to rise. Hence an estimation of the size of the rotating unit is considered interesting in this case.

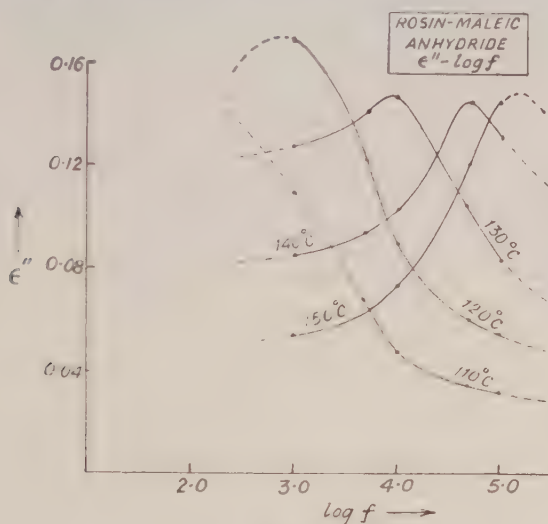


Fig. 5

The radius of the rotating unit was estimated from the calculated relaxation time at the temperature of loss maximum corresponding to a particular frequency and the melt viscosity at that temperature. The melt viscosity of this resin at

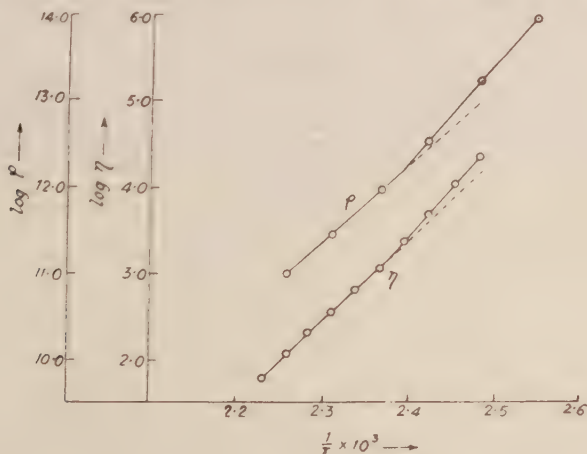


Fig. 6

different temperatures was measured by the same method as reported earlier (Sen and Bhattacharya, 1957) and the results are shown in Table I. Fig. 6 shows the logarithm of viscosity plotted against the reciprocal of absolute temperature and the graph is a straight line. For the sake of comparison the logarithm of resistivity is also plotted against the reciprocal of absolute temperature using the same scale. The conductivity and resistivity data appear in Table II. Once again the slopes of both these graphs are found to be the same. Upto the temperature of 170°C, however, none of these graphs shows any abnormality to indicate any likely polymerization within this temperature region.

TABLE I
Viscosity-temperature data

Temperature		$\frac{1}{T} \times 10^3$	Viscosity η in poise	log η
t°C	T°K			
130	403	2.481	22,970	4.3612
135	408	2.451	11,000	4.0414
140	413	2.421	4,900	3.6902
145	418	2.392	2,340	3.3692
150	423	2.364	1,200	3.0792
155	428	2.336	635	2.8028
160	433	2.309	355	2.5502
165	438	2.283	210	2.3222
170	443	2.257	120	2.0792
175	448	2.232	60	1.7782

TABLE II
D.C. conductivity or resistivity-temperature data

Temperature		$\frac{1}{T} \times 10^3$	Conductivity K in mho cm ⁻¹ .	Resistivity ρ in ohm cm.	log ρ
t°C	T°K				
120	393	2.545	0.1042×10^{-13}	9.596×10^{13}	13.9821
130	403	2.481	0.5970×10^{-13}	1.675×10^{13}	13.2240
140	413	2.421	0.2935×10^{-12}	3.407×10^{12}	12.5324
150	423	2.364	0.1067×10^{-11}	9.369×10^{11}	11.9717
160	433	2.309	0.3339×10^{-11}	2.894×10^{11}	11.4614
170	443	2.257	0.1036×10^{-10}	9.654×10^{10}	10.9847

The results of calculation of the radius of the rotating units are shown in Table III.

TABLE III
Calculated relaxation time and radius of the rotator

Frequency in kc/s	Loss maximum temperature t_m in °C	Relaxation time τ in sec.	$\log \eta$ at t_m	Radius of the rotator in Å
5	126	2.80×10^{-5}	4.60 (extra-polated)	1.45
10	131	1.39×10^{-5}	4.30	1.45
50	142	2.76×10^{-6}	3.60	1.46
100	147	1.39×10^{-6}	3.27	1.51

From these results we find again that the same value of the dimension of the hydroxyl group is obtained here for the radius of the rotator in this resin. We should examine therefore if there is any possibility for this resin of containing hydroxyl groups as probable rotating units. As in the production of this resin pentaerythritol is employed it is not unlikely for some of the four hydroxyl groups of the pentaerythritol molecule to remain unesterified in the same way as some hydroxyl groups of glycerol were found to remain unesterified in ester gum (Sen and Bhattacharya, 1958a) and copal ester (Sen and Bhattacharya, 1960). Moreover this possibility may also provide an explanation for the observed phenomenon of abnormal rise in permittivity above 150°C. For some of these hydroxyl groups may form hydrogen bonds amongst themselves at ordinary temperatures and these may be disturbed only at temperatures above 150°C. Consequently

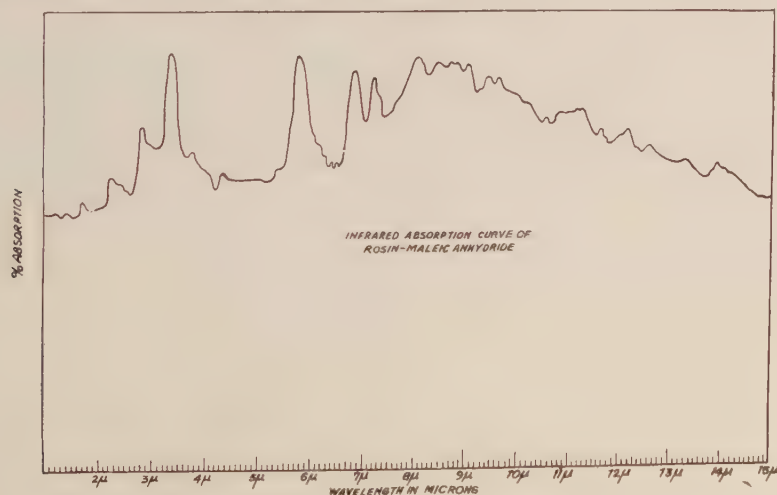


Fig. 7

upto 150°C only the free hydroxyl groups can contribute towards polarisation there being no contribution from the bonded hydroxyl groups. But at temperatures above 150°C these hydrogen bonds may break and the released hydroxyl groups may contribute further towards polarization thereby increasing the dielectric constant. Or, in the alternative there may be condensation-polymerisation above 150°C and the released water vapour may contribute towards increased dielectric constant.

The infrared absorption spectra of this resin was obtained in the manner indicated previously (Sen and Bhattacharya, 1960) and the spectrogram shown in Fig. 7. In this figure no absorption peak occurs at the wave length region of 2.93μ corresponding to the bonded hydroxyl group but the peak due to the free hydroxyl group occurs at about 2.78μ . The second explanation for increased values of dielectric constant above 150°C seems therefore reasonable. The free hydroxyl groups may be the unesterified hydroxyl groups of the pentaerythritol molecule as stated earlier. As chances of rotation of the entire resin molecule are remote, only side groups attached to the main molecule or segments of it are capable of orientation. Therefore hydroxyl groups attached to the molecule seem to be the probable rotating units.

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VIBRATIONAL SPECTRA OF THIOGLYCOLLIC ACID

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ABSTRACT. The infrared and Raman spectra of thioglycollic acid and its solutions in different solvents have been recorded and the assignments of some of the frequencies have been proposed.

INTRODUCTION

The Raman spectrum of thioglycollic acid has been earlier reported by Thatte and Ganesan (1933), but these authors have not recorded any line in the region of 2500 cm^{-1} corresponding to S-H stretching vibrations. Hibben (1936) while discussing the Raman spectra of thioacids, interpreted the absence of a line in the region of 2500 cm^{-1} in these compounds, as due to the absence of S-H group. There appears to be no mention in literature regarding the studies of infrared spectrum of thioglycollic acid. The authors have studied the infrared and Raman spectra of the acid and in various solvents in order (a) to assign the various vibrational frequencies of the monomer and associated molecules and (b) to study the effects of the solvents on the frequencies of the O-H, S-H and C = O stretching absorption bands.

EXPERIMENTAL

A Perkin-Elmer Model 21 Infrared Spectrophotometer with NaCl optics was used to obtain the infrared spectra. The infrared spectrum of the pure liquid was obtained by pressing a drop of the liquid between two NaCl plates, along with an NaCl plate of equivalent thickness inserted into the reference beam. The spectra in solutions were obtained with a pair of matching cells of 0.1 and 1 mm thickness.

The Raman spectra were obtained by using a Fuess glass spectrograph having a dispersion of 19 cm^{-1} in the $\lambda 4358$ region along with a Hilger Raman source unit. $\lambda 4358$ was the exciting radiation.

Thioglycollic acid (E. Merck) was distilled under reduced pressure and the fraction collected at 123°C and 29 mm pressure was used for the investigation. The fact that this acid forms an aqueous mixture of constant boiling point has been noted and absolutely anhydrous acid was used in the investigations.

RESULTS

The Raman and infrared frequencies of thioglycollic acid as recorded by the authors are given in Table I. The Raman spectrum reported by Thatte and Ganesan is given for comparison. The microphotometric trace of the Raman spectrum is given in Fig. 1. The infrared spectrum of thioglycollic acid has broad absorption band in the 3μ region, but this band could be resolved into three peaks in solutions of chloroform and carbon tetrachloride. The Raman spectrum of thioglycollic acid has a sharp and intense line in the region of 2500 cm^{-1} while the corresponding infrared band is weak. The authors could record a number of Raman lines which have not been reported earlier (Thatte and Ganesan, 1933).

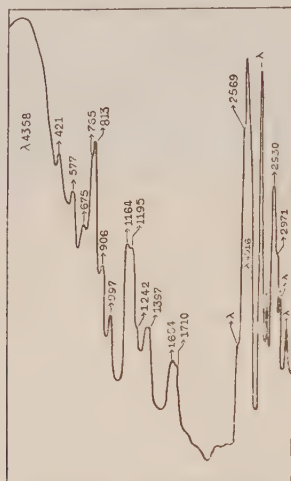


Fig. 1. Microphotometric trace of the Raman spectrum of thioglycollic acid.

DISCUSSION

Assignments :

The infrared spectrum of thioglycollic acid has a broad absorption band extending from 3125 cm^{-1} to 2900 cm^{-1} , but in solutions of chloroform it could be resolved into three distinct peaks at 3495 , 3125 and 2900 cm^{-1} . With increasing dilution, the intensity of the band at 3125 cm^{-1} becomes less and at 0.02 molar concentrations, this band becomes very feeble while the one at 3495 cm^{-1} is prominent. A characteristic feature of carboxylic acids is their dimeric manifestation, with the result that the intermolecular associations break up progressively with increasing dilution of these substances in chloroform or carbon tetrachloride. Therefore the authors assign the band at 3495 cm^{-1} to the free O-H stretching vibrations of the monomers and the one at 3125 cm^{-1} to the same mode of vibrations of the associated molecules. The Raman line which is assigned

to the bonded O-H stretch, has a banded structure extending from 2926 to 2971 cm^{-1} . A sharp intense Raman line appears at 2930 cm^{-1} superposed on the hydroxyl band. The band at 2900 cm^{-1} in the infrared or the one at 2930 cm^{-1} in the Raman spectrum is assigned to C-H stretching vibrations.

The C = O stretching absorption of thioglycollic acid has two peaks at 1717 and 1730 cm^{-1} , the former being a weak shoulder. The carbonyl frequency in the Raman spectrum appears as a band at 1654 cm^{-1} along with a sharp, faint line at 1710 cm^{-1} . These results indicate that the thioglycollic acid is not a completely associated liquid. With increasing dilution of the acid in chloroform, the peak at 1730 cm^{-1} becomes more prominent in the infrared spectrum and the band at 1717 cm^{-1} becomes a shoulder. At a molar concentration of 0.02 in solution of chloroform, only the band at 1730 cm^{-1} could be recorded. Therefore the infrared frequency at 1717 cm^{-1} or the Raman line at 1654 cm^{-1} is assigned to the C = O stretching of the associated molecules and the frequency at 1730 cm^{-1} in the infrared or the one at 1710 cm^{-1} in Raman spectrum to the same mode of vibrations of the monomers. The large differences in the infrared and Raman frequencies of the C = O stretch of the thioglycollic acid are in agreement with similar results obtained by Davies and Sutherland (1938) in their investigations of carboxylic acids.

The lines at 1298 and 1397 cm^{-1} in the Raman and the corresponding frequencies at 1286 and 1412 cm^{-1} in the infrared can be assigned to C-O stretch

and $\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{OH} \end{array}$ deformation. Such assignments have been made by Hadzi and

Sheppard (1953) in case of carboxylic acids and by Puranik (1955) in case of esters.

The Raman spectrum of thioglycollic acid has a sharp and intense line at 2569 cm^{-1} and the corresponding frequency in the infrared is a weak absorption at 2565 cm^{-1} . The authors assign this band to S-H stretching vibrations. The frequency remains unchanged even in dilute solutions of chloroform. This invariance of the frequency indicates that S-H linkage is a free linkage in thioglycollic acid. The intermolecular associations in this compounds, may therefore be concluded, as of O-H.....O = C type.

The S-H in-plane deformation frequency has been identified by Sheppard (1949) with a Raman line at 832 cm^{-1} and therefore the Raman line at 813 cm^{-1} in the thioglycollic acid may be assigned to this mode of vibration. The C-SH stretch is known to appear in the region of 600-700 cm^{-1} as a strong line in The Raman spectrum (Sheppard, 1950) and therefore a fairly intense Raman line at 675 cm^{-1} may be assigned to C—SH stretching vibrations.

The 220 cm^{-1} in the Raman spectrum corresponds to the symmetrical vibrations of the two acid molecules of the dimer through the stretching of the hydrogen bond.

TABLE I
Raman and infrared frequencies of thioglycollic acid
(in cm^{-1})

Raman		Infrared
Present authors	Thatte and Ganesan	Present authors
220 (0)	—	—
421 (2)	433 (1d)	—
—	511 (1)	—
577 (2)	580 (1)	—
675 (3)	686 (0)	—
765 (4)	—	755 (w)
813 (6)	818 (4)	—
906 (4)	914 (2)	897 (w)
997 (4)	1004 (0)	990 (vw)
1164 (5)	—	1149 (m)
1195 (3)	—	1199 (m)
1242 (3)	—	—
1298 (0)	—	1286 (s)
1397 (3)	1409 (2d)	1412 (s)
—	1563 (1d)	—
1654 (3d)	—	1717 (s)
1710 (1)	1707 (1d)	1730 (sh)
—	—	2336 (w)
2459 (2)	—	—
2569 (8)	—	2565 (w)
2678 (2)	—	2680 (sh)
2930 (9)	2950 (1d)	—
2926 to 2971	—	2930 to 3125

TABLE II

O—H, S—H and C = O stretching frequencies of thioglycollic acid in different solvents

Solvents	O—H stretch	S—H stretch	C—O stretch
Liquid	2930 to 3125	— 2565	— 1717 1730
Carbon tetrachloride	3510	2575	1718 1731
Chloroform	3500	2565	1717 1730
Acetonitrile	3450	2565	1742
Dioxane	3450	2535	1745
Pyridine	3225	2440	1717 (sh) 1730
α -picoline	—	2440	1709 1724
β -picoline	—	2440	1717 1730

Solvent effect.

The infrared spectrum of thioglycollic acid has been recorded in various solvents and the OH, SH and C = O stretching frequencies in those solvents are given in Table II and the traces are given in Figs. 2 and 3.

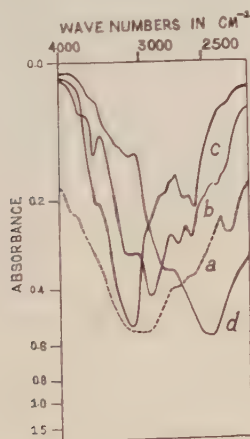


Fig. 2. The O—H, and S—H stretching frequencies in (a) pure liquid (b) chloroform (c) dioxane and (d) pyridine.

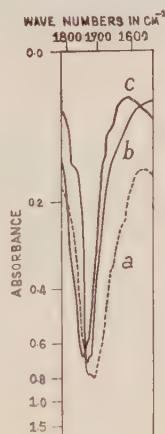


Fig. 3. The C=O stretching frequencies in (a) pure liquid (b) chloroform and (l) dioxane.

The absorption band at 3495 cm^{-1} in chloroform or at 3510 cm^{-1} in carbon tetrachloride, which is assigned to the O—H stretch of the monomers, does not appear in the donor solvents. Instead it appears at 3450 cm^{-1} in dioxane and acetonitrile and at 3225 cm^{-1} in solutions of pyridine. At these concentrations the carbonyl frequency is at 1743 cm^{-1} in both dioxane and acetonitrile. In pyridine it is at 1730 cm^{-1} with a weak shoulder at 1717 cm^{-1} . Similar results are obtained in solutions of picolines.

The appearance of a single $\text{C}=\text{O}$ absorption in the donor solvents corresponding to the monomer frequency is an indication that the intermolecular associations have broken up considerably in these solvents. Then the simultaneous reduction in the O—H stretching frequency compared to the monomer frequency in solutions of chloroform or carbon tetrachloride is due to the hydrogen bond formation between the donor groups of the solvent and the O—H group of the monomers of the acid by the $\text{OH}\cdots\text{N}$ and $\text{OH}\cdots\text{O}$ bonds. The shift in the O—H stretching frequency is maximum in solutions of pyridine.

The S—H stretching frequency, which has the same value in pure liquid and in dilute solutions of chloroform, decreases to the extent of 125 cm^{-1} in solutions of pyridine and picolines and becomes broad. In solutions of dioxane this band shifts only to the extent of only 25 cm^{-1} . The large shifts in S—H stretching frequency in solutions of pyridine and picolines, may be concluded as due to the associations by way of $\text{S—H}\cdots\text{N}$ bonding.

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STUDIES ON BINARY DIFFUSION OF THE GAS PAIRS

 N_2 -A, N_2 -Xe AND N_2 -He

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ABSTRACT. The mutual diffusion coefficient of N_2 -He, N_2 -Xe and N_2 -A gas pairs over the temperature interval -30°C to 60°C has been determined by allowing the diffusion to take place between two bulbs through a precision capillary tube. Samples of the gas, withdrawn from one of the bulbs at different times, were analysed by using a previously calibrated thermal conductivity analyser. These experimental data have been utilised for calculating the unlike potential parameters on the Lennard-Jones 12 : 6 model. The parameters have been used to calculate D_{12} and are found to reproduce the experimental data satisfactorily. Further, the thermal conductivity of the mixtures is calculated using only the experimental values of D_{12} and other transport properties of pure gases and reasonable agreement with the experimental data is obtained.

INTRODUCTION

The coefficient of mutual diffusion, D_{12} is the most suitable transport property for studying unlike molecular interactions, because, to the first approximation, it depends only on the force field of the unlike molecules. But the experimental data suitable for inter-molecular force determination are scanty, specially for the poly-atomic molecules. Therefore, mutual diffusion data for various pairs of gases are most desirable. With this end in view a series of accurate diffusion coefficient measurements of different gaseous mixtures have been done in this laboratory over a fairly wide range of temperature. Several workers (Srivastava and Srivastava, 1959a, Srivastava, 1959, Srivastava and Barua, 1959) have measured the binary diffusion of inert gases in the temperature range 0°C - 45°C by using the two-bulb diffusion method and have used their data to determine the unlike interaction parameters on the Lennard-Jones (12 : 6) model. The same technique was further used by Paul and Srivastava (1961a, 1961b) for measuring D_{12} of binary mixtures containing a diatomic gas, in the temperature range -30°C to 60°C . In the present work, the mutual diffusion coefficients of N_2 with He, A and Xe have been measured in the above temperature range and the experimental data are used for determining the force constants for unlike interaction on the Lennard-Jones (12 : 6) model.

APPARATUS AND THEORY

The two-bulb technique of Ney and Armistead (1947) was employed for measuring the diffusion coefficients. The details of the apparatus, experimental

procedure and the theory have been discussed fully by Paul and Srivastava (1961a).

EXPERIMENTAL RESULTS

The gases used were supplied by British Oxygen Company, England and were quoted to be spectroscopically pure, except xenon which contained about 1% krypton.

Constants of the diffusion apparatus :

Volume of bulb I	325 cc.
Volume of bulb II	547 cc.
Length of the diffusion capillary	9.058 cm.
Diameter of the diffusion capillary	0.316 cm.

$$C_1^{\infty} = 0.373,$$

C_1^{∞} is calculated from the initial concentration in the two bulbs, which was further checked for some runs by determining the concentration at an interval of seven times the relaxation time.

TABLE I

Observed concentration of He at different times for N₂-He at -30°C

Time in minutes	R in ohms	C_1^t	$C_1^t - C_1^{\infty}$	$\log_{10}(C_1^t - C_1^{\infty})$
0	—	1.000	0.627	1.7973
35	235.8	0.770	0.397	1.5988
51	229.4	0.691	0.318	1.5024
71	222.8	0.616	0.243	1.3856
91	217.1	0.559	0.186	1.2695

Fig. 1 gives the calibration curve for the three gas pairs and Fig. 2 shows the plots of $\log_{10}(C_1^t - C_1^{\infty})$ versus t for N₂-He at all temperatures.

Table II gives the experimental values of diffusion coefficients for different pairs as determined by the present authors, together with the values obtained by other workers, wherever available, and also the calculated values of D_{12} , using the force constants obtained by the authors.

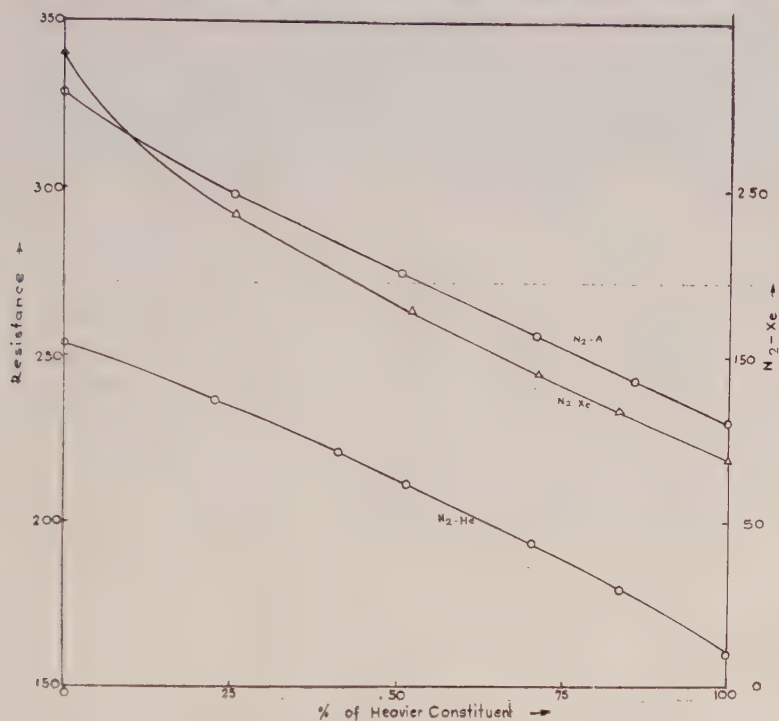


Fig. 1. Calibration curves.

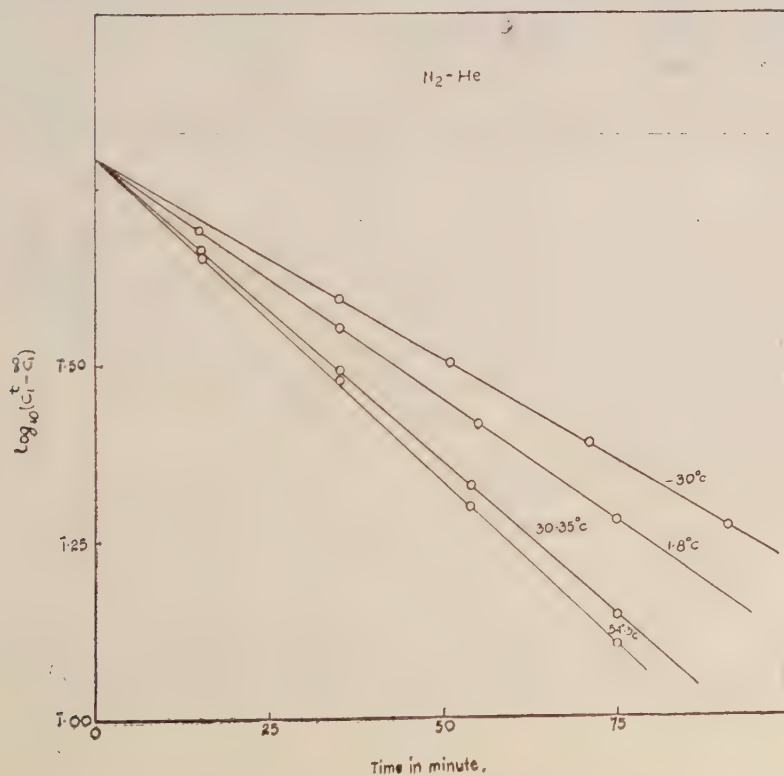


Fig. 2. Plot of $\log (C_1^t - C_1^\infty)$ versus 't' for N_2-He .

TABLE II

Observed values of the diffusion coefficient in cm²/sec

Gas mixtures	Temp. °K	Pressure in mm. Hg.	D_p	$D_{atm.}$	Previous ^a work	D_{12} calc. from force constants fitted to diffusion data
N ₂ -He	243.2	62.0	5.847	0.477		0.484
	275.0	64.5	7.022	0.596		0.597
	298.16	—	—	—	0.7068	0.6797
	303.55	62.1	8.799	0.719	—	0.704
	328.16	—	—	—	0.8212	0.8011
	332.5	65.5	9.410	0.811	—	0.819
	358.16	—	—	—	0.9410	0.9232
N ₂ -Ar	244.2	64.7	1.583	0.1348		0.1363
	274.6	62.2	2.063	0.1689		0.1685
	303.55	64.5	2.355	0.1999		0.2018
	334.7	68.3	2.707	0.2433		0.2399
N ₂ -Xe	242.2	63.2	1.027	0.0854		0.0854
	274.6	64.4	1.262	0.1070		0.1078
	303.45	70.0	1.413	0.1301		0.1299
	334.2	60.3	1.952	0.1549		0.1551

^a Rumpel, W.F. (1955)

DETERMINATION OF POTENTIAL PARAMETERS

The various methods for determining the potential parameters from the measured D_{12} values have been fully discussed by Bunde (1955) and Srivastava and Srivastava (1959a), pointing out their advantages and limitations. In the present work, the intersection method of Buckingham (1937) has been used for the determination of the force constants on the Lennard-Jones (12:6) model. As some scatter was found in the intersection points of the curves, the force constants obtained by this method were considered as approximate ones. These approximate values were used to calculate the parameters more accurately by the method of least square fitting. The least square method followed here has been discussed in detail by Paul and Srivastava (1961b).

The force constants determined are tabulated in Table III, together with the values obtained from the combination rules. It is clearly seen that the two sets of force constants agree within the limits of experimental error.

TABLE III

Potential parameters on the Lennard-Jones (12:6) model from the experimental data

Gas pair	Present work	From combination rules
N_2-He		
ϵ_{12}/k ($^{\circ}K$)	35.44	30.58
σ_{12} (\AA)	3.129	3.129
N_2-A		
ϵ_{12}/k ($^{\circ}K$)	107.03	106.5
σ_{12} (\AA)	3.530	3.549
N_2-Xe		
ϵ_{12}/k ($^{\circ}K$)	147.4	144.8
σ_{12} (\AA)	3.846	3.868

COMPARISON WITH EXPERIMENTS

(a) *Mutual diffusion coefficient*

The force constants obtained in the present work have been used to calculate the diffusion coefficients, which have been tabulated in Table II. The agreement obtained is excellent. Further, in case of N_2-He where data of other workers (Rumpel, 1955; Walker and Westernberg, 1958) are available upto $1100^{\circ}K$, the diffusion coefficients calculated from our force constants have been compared

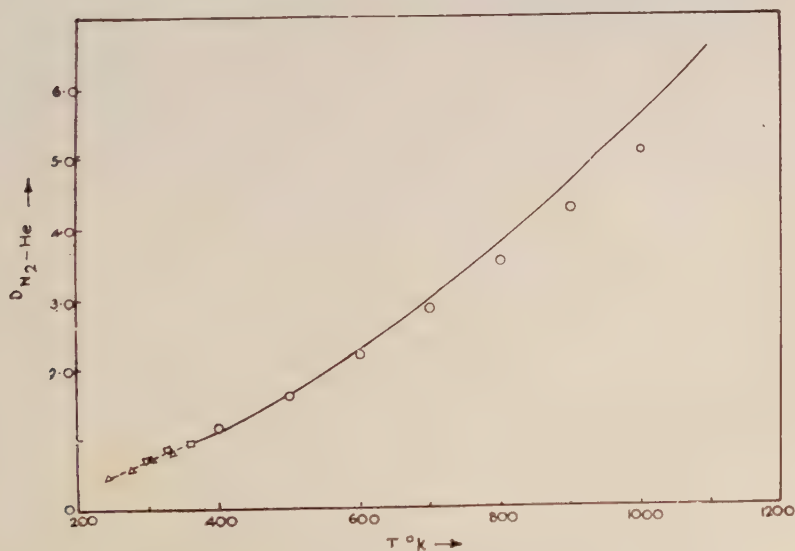


Fig. 3, Temperature variation of the diffusion coefficient of N_2-He system.

— Interpolated from Walker and Westernberg (1958)

Δ Present work. \square Data taken from Rumpel (1955).

\circ Calculated values using force constants obtained in the present paper.

graphically with experimental values in Fig. 3. It will be seen from the figure that up to 700°K, the force constants obtained here reproduce experimental values tolerably well. At higher temperatures there are significant deviations, but the force constants determined from the data in the temperature range 250°K to 350°K are not expected to hold good above 700°K.

(b) *Thermal conductivity of mixtures*

The full procedure for the determination of the thermal conductivity of mixtures from the experimental values of the mutual diffusion coefficient and other transport properties of pure component has been given previously (Paul and Srivastava, 1961a).

Fig. 4 presents the experimental values of the thermal conductivity of the mixtures with those calculated by the above method. The agreement is excellent for all the three mixtures. The experimental values of thermal conductivity are taken from Srivastava and Srivastava (1959b) for N_2 -A and from Barua (1959) for N_2 -He and N_2 -Xe.

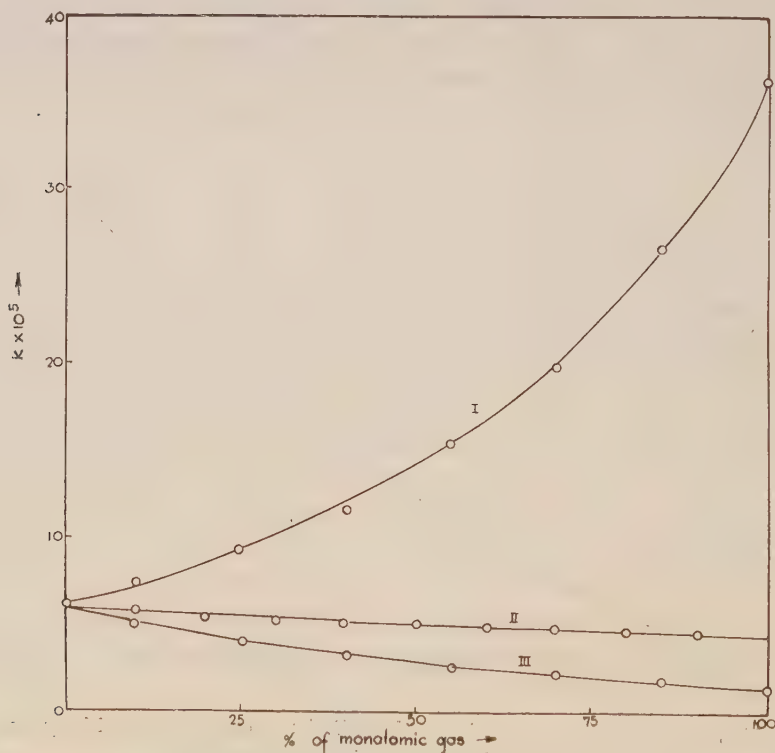


Fig. 4. Comparison of experimental and calculated values of thermal conductivity.
I. E_2 -He at 30°C, II. N_2 -A at 38°C, and III. N_2 -Xe at 30°C.

DISCUSSIONS

As the force constants for the pure components are not known very accurately, it is not possible to test the combination rules critically. However, like previous cases, in the present work also, no systematic departure from the combination rule could be observed.

It will be of considerable interest to see how well our force constants reproduce the transport properties other than diffusion and thermal conductivity, but unfortunately, no such data are available at present.

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ELECTRON MICROSCOPE STUDIES ON THE COTTON CELLULOSE

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ABSTRACT Hydrolysis of cotton cellulose in strong mineral acid shows a disintegrating fibrillar structure under electron microscope. The broken up fibrils and particles have almost the same lateral dimension and there is an indication of layer lattice structure of cellulose. No definite minimum of the length of the particles could be observed.

INTRODUCTION

Morphological study of cotton cellulose by some workers (Balls and Hancock, 1922) under light microscope shows dislocated striations. Dislocation of striations were also noted in most of the bast fibres prominently in flax (Muhlethaler, 1949). The transverse section shows cell structure in both the varieties (Hock *et al.*, 1940). The molecular structure has been studied by X-ray and the unit cell has been defined (Hessler *et al.*, 1948). The state of orientation and purity of fibre, so far as α -cellulose content in fibre is concerned, has also been studied (Berkley *et al.*, 1938, 1949).

From the usual X-ray diagram and also from small angle scattering, the average length of cellulose crystallites of Remie was found to vary between 500 Å and 600 Å (Heyn, 1950). But the exact shape and locations of these crystallites in the fibre could not be ascertained for want of proper technique.

It will be observed that the size of crystallites as suggested from X-ray studies is within the range which could be advantageously studied under electron microscope. The early attempts to study the structure of cellulose with electron microscope by Ruska and others (1940) did not succeed. Subsequently, attempts by replica technique by Astbury and Preston (1948) indicated the fibrillar structure, while Freywisling (1948) using mechanical grinding reported fibrillar structure of varying width and length. Subsequently Ranbi and Ribi (1949 and 1951) and also Mukherjee and Woods (1953) tried acid hydrolysis for the disintegration of fibres. They were successful in breaking the fibrils into discrete particles, believed to be the crystallites of cellulose. The present work contains an account of the electron microscopic studies on Indian cotton cellulose using the acid hydrolysis technique developed by Mukherjee and Woods (1953).

EXPERIMENTAL PROCEDURE

In this work a sample of raw Indian cotton was dewaxed by soxhlate extraction with Carbon tetra-chloride and after drying, it was further purified by boiling in dilute (2%) sodium hydroxide solution for 4 hours. The purified fibre was next treated in sulphuric acid solution of strength 920 grammes per litre at 32°C. The fibres disintegrated into small fragments and dispersed in the acid. In an attempt to wash this material by distilled water in a centrifuge, the fibres dispersed still further in a colloidal solution at a pH round about 4. The colloidal solution obtained by peptisation at each washing in the centrifuge was collected. This acidic colloidal solution was then dialysed in cellophen bags in distilled water at room temperature. Four to five days had to be allowed in the process of dialysis to raise the pH of the solution to about 5.5. Because the pH of distilled water itself against which the solution was dialysed was 5.8. The dialysed solution was further diluted with distilled water in order to obtain a concentration suitable for electron microscope. The specimen for an electron microscope was obtained by putting a small drop of solution on a colloidion coated microscope grid and evaporating the water to leave the cellulose behind. The specimen was next shadowed with chromium and subsequently examined under electron microscope. The microscope used was Siemens' Elmiskop I at 60kV.

TABLE I

Obs. nos.	Width of individual particles on the micrograph (cm)	Actual width of individual particles (cm) \div 17000
1	1.96×10^{-2}	115.3×10^{-8}
2	2.91	171.2
3	1.97	115.9
4	2.89	170.0
5	1.79	105.3
6	2.13	125.3
7	2.06	121.2
8	1.82	107.1
9	2.83	166.5
10	1.81	106.5
Mean width = $130.4 \pm 8.70 \text{ \AA}$.		

DISCUSSION

The electron micrograph (Fig. 1) shows a distinct fibrillar structure with a definite indication of breakdown into elongated discrete particles as could be

seen in the field of observation. It is also observed on the micrograph that the fibrils and the particles have more or less the same lateral dimension. In other

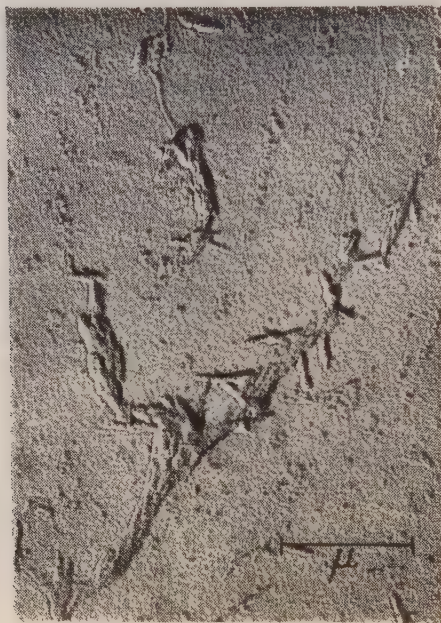


Fig 1.

words the structure as revealed under microscope shows a disintegrating fibrillar structure breaking into particles. On closer observation of the aggregates, there is an indication that they are rather in flat layers which probably are in conformity with the idea of layer lattice, associated with structure of cellulose. No definite minimum of the length of the particle could be observed. But they were found to vary from 500\AA to 2500\AA and above. Nevertheless the width of the particles was found to vary within a narrow range, when measured. The average width of the particle was found to be about $130.4 \pm 8.70\text{\AA}$.

It is expected that under favourable conditions, by using different time, concentration and temperature of acid it may be possible to study the individual units (fibrils) which is the basis of building mechanism of the structure. This work is being further pursued to see if similar results can be obtained in case of bast fibres and to study the difference, if any, between the bast fibres and comparatively more pure varieties of fibres like cotton and also amongst the bast fibres themselves.

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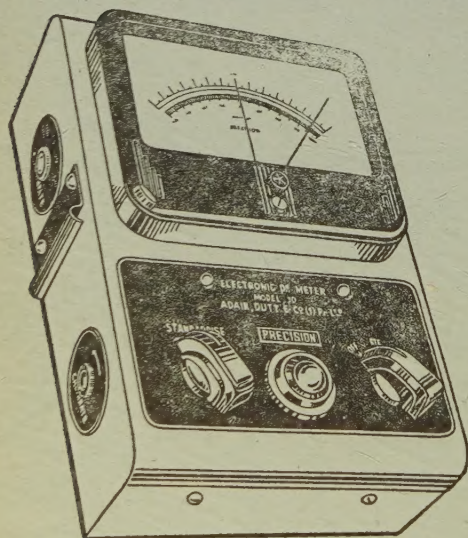
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